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PROTON NMR THERMAL SCANNING METHODS FOR THE STUDY OF OIL SHALE PYROLYSIS

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INTRODUCTION

Dynamic experimental techniques by which non-equilibrium states of a system can be observed during thermally induced transformations allow the kinetics of pyrolysis mechanisms to be directly studied. This paper reports on the novel use of simple low resolution Proton nuclear magnetic resonance (^1H NMR) measurements as a reaction time probe to monitor the state of oil shales during heating from room temperature to $\sim 870\text{K}$. The method involves the observation of the ^1H NMR transverse relaxation transient at regular intervals during heating. Similar studies of coal pyrolysis (1-6) and a description of the apparatus (7) used have been previously reported. In these reports, the ability to obtain non-equilibrium data during fossil fuel pyrolysis despite the limited scope for signal averaging and the deterioration of signal-to-noise of the ^1H NMR signal with rise in temperature was demonstrated.

The experiments reported here involved measurements of the ^1H NMR during pyrolysis of shale specimens contained in open tubes and flushed with dry nitrogen gas so that volatile pyrolysis products were quickly removed. A number of different parameters extracted from the data are investigated for their usefulness in monitoring changes that occur in the properties of the specimen. These parameters relate to the loss of hydrogen from the specimen and changes that occur in the molecular structure and mobility as a consequence of chemical and physical transformations.

The results presented are not part of a systematic study of oil shale pyrolysis but rather those of various experiments selected to demonstrate the utility and potential of the method.

EXPERIMENTAL

The shale samples used here were obtained from CSIRO Division of Fossil Fuels and CSIRO Division of Energy Chemistry in a finely ground form. The specimens for measurement consisted of 300-500 mg of material predried under nitrogen at 105°C and contained in open glass tubes. The ^1H NMR measurements were made at 60 MHz or 90 MHz using high temperature specimen probes and temperature control apparatus described previously (7). The specimens were positioned within the inner 2/3 of the measurement radio-frequency coil of the NMR probe so that at all stages during an experiment the ^1H NMR signal of all the residual material was recorded. The specimen tubes were continuously flushed with a stream of dry nitrogen gas throughout the heating cycles which rapidly removed volatile products formed from the measurement zone.

The $90^\circ\text{-}\tau\text{-}90^\circ$ NMR pulse sequence (8) was used to stimulate the solid-echo ^1H NMR transverse relaxation signal as shown in Figure 1. This method of observing the signal is preferred to the simpler single 90° pulse method to overcome the receiver dead-time problem which is significant for many of the rapidly relaxing ^1H NMR transients observed. Receiver dead-time was $\sim 4\mu\text{s}$ and a pulse spacing, τ , of $15\mu\text{s}$ was used.

Measurements were recorded dynamically at regular intervals while the specimens were heated at a uniform rate of $4\text{K}/\text{minute}$ from room temperature to temperatures greater than 850K . Temperatures were recorded with an accuracy of $\pm 1\text{K}$ and care was taken to maintain tuning of the NMR probe during the changing conditions of the experiment. A Bruker BC-104 transient digitizer carefully compensated for spurious signals was used to record the ^1H NMR solid-echo signals.

RESULTS AND ANALYSIS

A typical ^1H NMR solid-echo signal recorded during heating is shown in Figure 1. For a rigid-lattice pair-wise dipolar coupled population of proton spins, the solid-echo signal is a full representation of the transverse relaxation and the peak of the echo, i_T , a measure of the total hydrogen content of the specimen (8). The extent to which the proton populations of the heated oil shales deviate from such a model will vary in a complex way during pyrolysis and we expect a

corresponding variation in the recorded ^1H NMR signals which, therefore, cannot be strictly considered in terms of the theory for a pair-wise dipolar coupled solid. It is expected that deviations from the model will occur because of multiple proton dipolar interactions, the variable degree of molecular mobility that occurs and the occurrence of dipolar interactions with paramagnetic species during pyrolysis. Details of how these factors affect the solid-echo experiment have been considered to some extent by others (8, 9).

The experimental echo peaks that are clearly visible for pulse spacings of $\tau = 15\mu\text{s}$ (Figure 1), however, occur 2-3 μs earlier than the 31 μs predicted if the systems behaved ideally. This discrepancy is consistent with the facts that when the specimens exhibit purely 'rigid-lattice' behavior, the condition $\tau \ll T_2$ does not hold, where T_2 is the transverse relaxation time and that under other conditions the specimens are not ideally dipolar coupled solids.

In this analysis, we interpret the experimental results as true solid-echoes but discuss implications of deviations from the assumed model where appropriate.

The echo peak height, i_T , is chosen as a measure of the total hydrogen remaining in the residue at any given time during pyrolysis. Because the sensitivity of the ^1H NMR signal of a population of spins is inversely related to some power of the temperature (10), it is necessary to apply an amplitude correction to the measured values of i_T . An empirical temperature calibration of the experimental probe was made using a coal char specimen sealed in a glass ampoule. This material had been previously pyrolysed at a temperature of greater than 950K and besides having a constant hydrogen content, appears relatively constant in its ^1H NMR properties over the temperatures of the calibration (i.e. 300-770K). The ^1H NMR signals for a Glen Davis oil shale observed dynamically at four temperatures during heating are shown in Figure 2. These ^1H NMR data have been compensated for temperature dependence using the coal char calibration so that the echo peak amplitudes, therefore, represent the apparent hydrogen contents. This calibration has been found qualitatively successful when applied to the data of a number of coal pyrolysis experiments (5, 6) but when used for most oil shale experiments, an anomaly occurs in that there is an initial increase in the apparent hydrogen content on heating above room temperature. This anomaly can be seen in the plots of the temperature dependencies of the apparent hydrogen content for both a whole and a demineralized Julia Creek oil shale (Figures 4 and 5) and for a Glen Davis oil shale (Figure 3). This anomaly is not so apparent if the magnetic field is made inhomogeneous so that the transient ^1H NMR signals are always rapid and independent of the specimen's nature. However, we suspect this anomaly is related to the presence of paramagnetic species in the specimens and the fact that it occurs greatly reduces the quantitative usefulness of this method of hydrogen content determination. It, nonetheless, is very useful for at least qualitatively defining the main pyrolysis regions at higher temperatures, where there is a rapid loss of hydrogen. Numerical differentiations of these data (Figures 3-5) show the temperature region of maximum rate of '% hydrogen loss'. These 'hydrogen loss' scans are analogous to thermogravimetric analysis and in the several instances where parallel measurements have been performed, similar temperature regions have been observed for the maximum rates of 'hydrogen loss' and weight loss, respectively.

Besides detecting thermal decomposition of the specimen, these ^1H NMR signals clearly indicate changes that occur in the state of the specimen during pyrolysis. It is useful to postulate that, at all stages of pyrolysis, the organic material contains both 'rigid' hydrogen with a rapidly relaxing ^1H NMR transient and 'mobile' hydrogen with a relatively slower relaxing transient. We have attempted to make such a distinction by resolving the observed transients into two components. The procedure for doing this is to a large extent arbitrary and the accuracy to which a particular method can be applied varies greatly with the condition of the specimen. The method we have used is to fit an exponential $-i_m \exp(-t/T_2^*)$ - to the tail of the transients where it is assumed only the 'mobile' slowly relaxing protons are represented. This method of analysis is outlined in Figure 1. From this analysis, two parameters are obtained: (i) the percentage of the residual hydrogen in the 'rigid' state - i.e.

$$i_R \% = \left(\frac{i_T - i_m}{i_T} \right) \times \frac{100}{1}$$

and (ii) the time constant T_2^* of the 'mobile' hydrogen component of the ^1H NMR transient. The results of such analyses of pyrolysis data for Glen Davis, Julia Creek and Julia Creek demineralized shale specimens are shown in Figures 6, 7 and 8, respectively.

A parameter that has been widely used in the study of the structure and thermal properties of solid organic materials (11-13) and particularly coals (12, 14) is the ^1H NMR second moment. To compute such a parameter from our solid echo data requires its Fourier transformation from the time domain to obtain a complex frequency domain ^1H NMR spectrum, i.e. $g'(\omega) = u'(\omega) + iv'(\omega)$. The quadrature components of this spectrum represent linear combinations of the pure absorptive ($u(\omega)$) and dispersive ($v(\omega)$) modes of the true spectrum, i.e.,

$$u'(\omega) = v(\omega)\cos\theta + u(\omega)\sin\theta$$

$$v'(\omega) = v(\omega)\sin\theta + u(\omega)\cos\theta$$

where θ (ω) is a frequency dependent phase shift nominally resulting from an error in the zero of time in the time domain data. For our data, its value is determined by the time selected for the solid-echo peak which is uncertain to varying degrees. It is usual to empirically adjust the phase relationship to separate the absorptive and dispersive modes. However, because the usual second moment parameter is critically dependent on this adjustment, we have instead computed the power spectrum given by

$$a(\omega) = u'(\omega)^2 + v'(\omega)^2$$

which is independent of the phase error. Such power spectra computed for the Glen Davis solid echo transients shown in Figure 2 are shown in Figure 6. Echart and Wroblewski (15) have demonstrated the validity of using this power spectrum rather than the absorption spectrum for line shape analysis in high resolution spectroscopy. We have, therefore, computed a second moment parameter, M_2^* , of the power spectrum defined as

$$M_2^* = \int_{\omega_0}^x a(\omega) \Delta\omega^2 d\omega / \int_{\omega_0}^x a(\omega) d\omega$$

where ω_0 is the central resonance frequency, $\Delta\omega = (\omega - \omega_0)$ and the limit of integration, x , is chosen to be at a frequency where $a(\omega) = a(\omega_0)/10$. Truncation at this value of x has been chosen by trial as a compromise between increased random errors that accrue for smaller values and the increase in systematic errors that result from greater truncation. We have found that the temperature dependence of M_2^* computed for this truncation is qualitatively the same as for lesser truncations and most of the quantitative features are relatively the same.

Examples of the temperature dependence of M_2^* are shown in Figures 10, 11 and 12 for Julia Creek, Julia Creek demineralized shales and Glen Davis shale, respectively.

DISCUSSION

^1H NMR results presented here are unique in that they were obtained under the non-equilibrium conditions of temperature controlled pyrolytic decomposition of the shales. We have established experimental techniques that ensure good reproducibility of the changes manifest in these dynamically recorded ^1H NMR solid echo signals. By these techniques, it is possible to obtain a set of data characterizing a shale which we choose to call a ^1H NMR thermal scan'.

The analysis of the ^1H NMR thermal scan data has been in three parts:

(i) An intensity parameter, I_T , directly related to the hydrogen content of the residual, has been used to monitor the loss of volatile products and, thereby, detect the main region of pyrolytic decomposition.

(ii) The ^1H NMR signals have been resolved into two components according to a model that distinguishes two phases differing in molecular mobility. It should be emphasized that this division is, to a large extent, arbitrary and that although these analytical components are referred to as 'rigid' and 'mobile', respectively, the distinction is only relative and, in fact, the so called 'rigid' component need not be that of a truly rigid-lattice structure. Also obtained by this method of analysis is a parameter, T_2^* , which is the time constant of the 'mobile' component of the ^1H NMR transient. This is a measure of the average molecular mobility of the 'mobile' material - the greater the average mobility, the greater the value of T_2^* . It is expected that, as the temperature is raised, a number of different factors would, therefore, influence the value of T_2^* - (a) the rate of transformation of material from the 'rigid' to the 'mobile' state, (b) thermal activation and/or breakdown of the 'mobile' molecules, (c) the rate of loss by volatilization of presumably the smaller and more mobile of the molecules and (d) at higher temperatures, the formation of the rigid residue from the 'mobile' material.

(iii) The second moment of the power spectrum, M_2^* , has been derived as a parameter which monitors the changes in the structural composition and mobility of the material that are manifest in the total line shape function of the ^1H NMR signals. Low temperature ($\sim 70\text{K}$) ^1H NMR second moments, measured for the frequency spectrum rather than for the power spectrum, have been used to estimate the chemical composition of coals (14). This is because the second moment of the coal can be defined as the weighted average of the second moments of all the constituent groups. For a rigid-lattice solid, each chemical group can be assigned a characteristic second moment

which is a measure of the dipolar interactions and, therefore, critically dependent on the interproton distances. Of particular significance is the fact that the second moment values for rigid lattice aliphatic structures are about three times those typical of aromatic structures (12, 14). The dipolar interactions of reorienting molecular groups are greatly reduced by the motion so that the groups no longer significantly contribute to the overall second moment of the specimen. Thus, by monitoring this normally used second moment of the frequency spectrum or the closely related parameter, M_2^* , used by us, we witness the thermally induced changes both in the chemical composition of the shale and the net molecular mobility of the constituent groups. It should be noted, that to the extent that this parameter is a measure of the average molecular mobility of the total specimen, its value is dominated by the more rigid components.

Although each of the three methods of analysis is subject to uncertainty in interpretation and precision of measurement, they separately and in combination provide much novel information on the processes involved in shale pyrolysis.

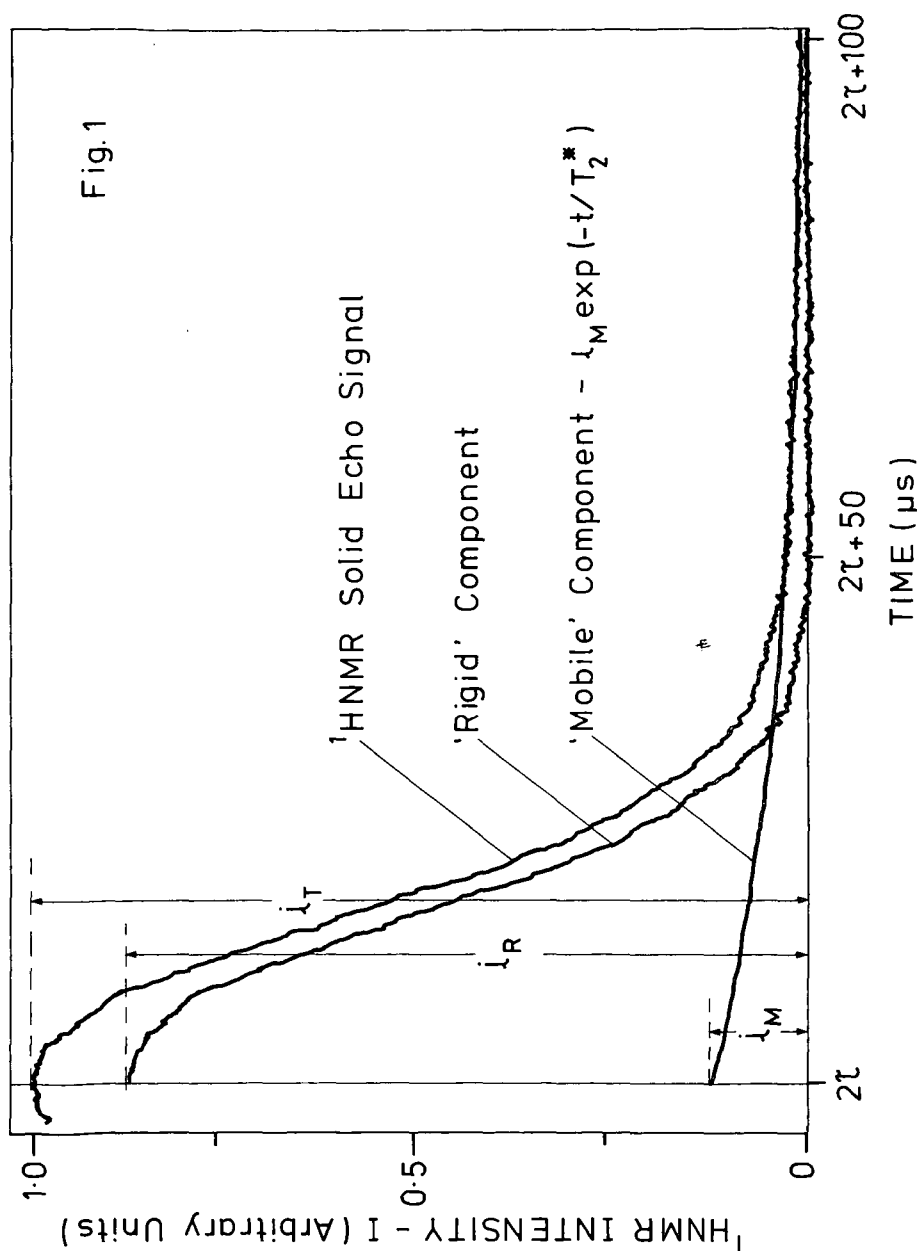
From the apparent hydrogen content and differential hydrogen content data for the Glen Davis shale (Figure 3), it is seen that rapid thermal decomposition and loss of volatile material occurs during a clearly defined period between 700 and 800K. In the course of heating, it is seen that there is a steady conversion of hydrogen from the 'rigid' to the 'mobile' state (Figure 7) and that this process seems to occur in two stages. The first stage occurs between room temperature and 660K and the second and more rapid conversion between 660K and 720K by which time all of the material is in the 'mobile' state. This is reflected in the temperature dependence of M_2^* (Figure 12). At 720K, M_2^* attains a very small value consistent with the absence of any significant amount of rigid-lattice hydrogen. Between 720K and 800K and accompanying the rapid loss of volatile hydrogen from the specimen, a rigid residue is formed which contains more than 10% of the total hydrogen and has a M_2^* value consistent with it being a rigid-lattice, aromatic material. Beyond 800K, the decrease in M_2^* is evidence of molecular 'softening' in this residue. We have observed this same phenomenon for bituminous coals and more particularly in an inertinite concentrate but not for a vitrinite concentrate.

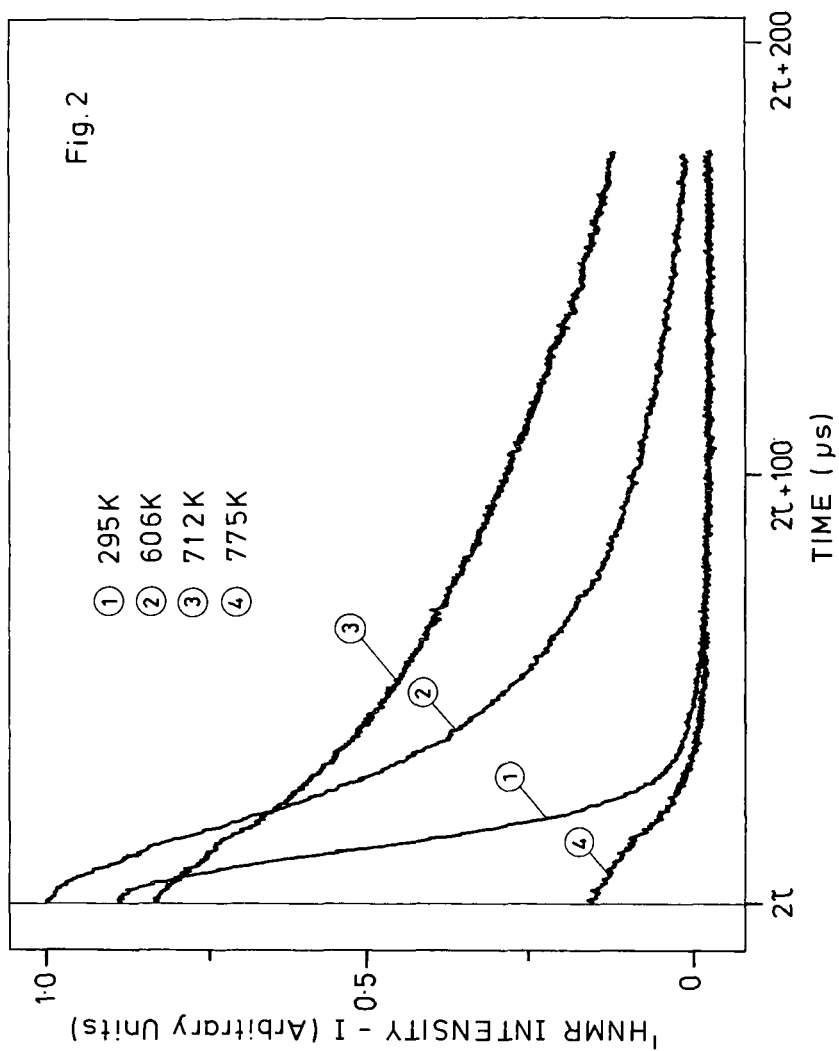
The behavior of the T_2^* parameter reflects its rather complex nature but the well defined maximum which occurs near the temperature of maximum rate of hydrogen loss (Figures 3 and 7) is the result of the competing processes of molecular breakdown and thermal activation on the one hand and the loss of mobile material by volatilization and conversion to the rigid residue on the other.

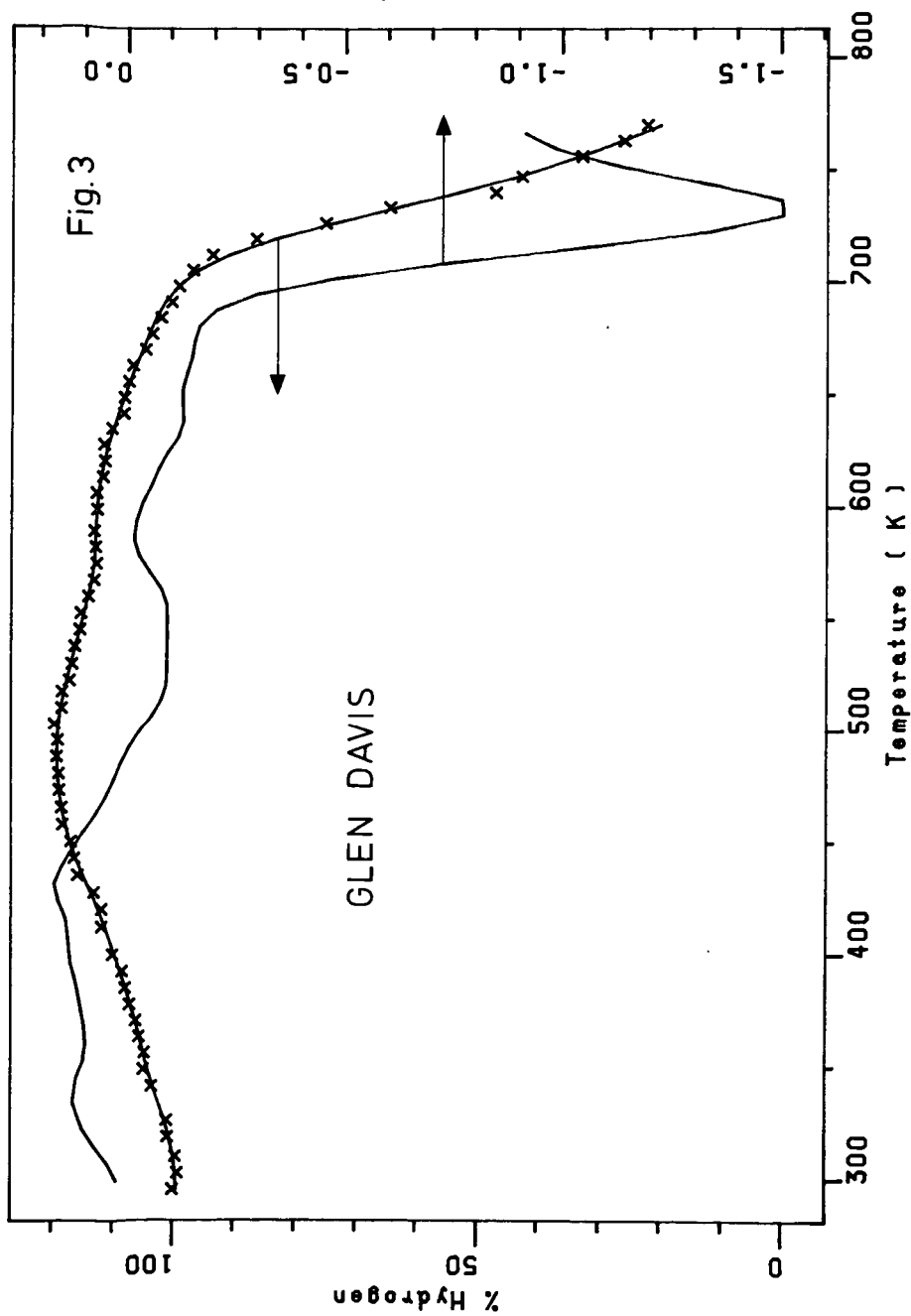
The ^1H NMR thermal scanning data for the Julia Creek shale and demineralized shale are similar to each other but are quite different from those of the Glen Davis shale. Compared to the data for the Glen Davis shale, we note the following general differences for the Julia Creek materials. (a) The onset of thermal decomposition is not as sudden (Figures 4 and 5) and the major zones of thermal decomposition as indicated by the apparent hydrogen loss and differential hydrogen loss occur at significantly lower temperatures. Also, the temperatures of maximum rate of percentage hydrogen loss occur at significantly lower temperatures and these rates are significantly less. (b) There is little change in the molecular mobility of the Julia Creek specimens below 450K as indicated by changes in either M_2^* (Figures 10 and 11) or the proportion of 'rigid' hydrogen (Figures 8 and 9) but beyond 450K, the rate of molecular 'mobilization', as revealed by these parameters, proceeds more rapidly. Whereas M_2^* reaches a very small minimum value indicating the absence of any rigid lattice component in the materials at a lower temperature than for the Glen Davis shale, the minimum in the 'rigid' hydrogen content (Figures 8 and 9) only reaches 30-40% as compared to ~0% for the Glen Davis shale. This apparent contradiction can be explained by reference to the ^1H NMR solid echo signals which are not shown here. The ^1H NMR relaxation rates of the so called 'rigid' hydrogen fraction in this temperature region indicate that, although this material is considerably less mobile than the 'mobile' fraction, it is not, in fact, a rigid structure. (c) The formation of the rigid residues occur earlier and again in parallel with the loss of volatile material but a much greater fraction of the hydrogen remains in the residue (Figures 10 and 11 and Figures 4 and 5).

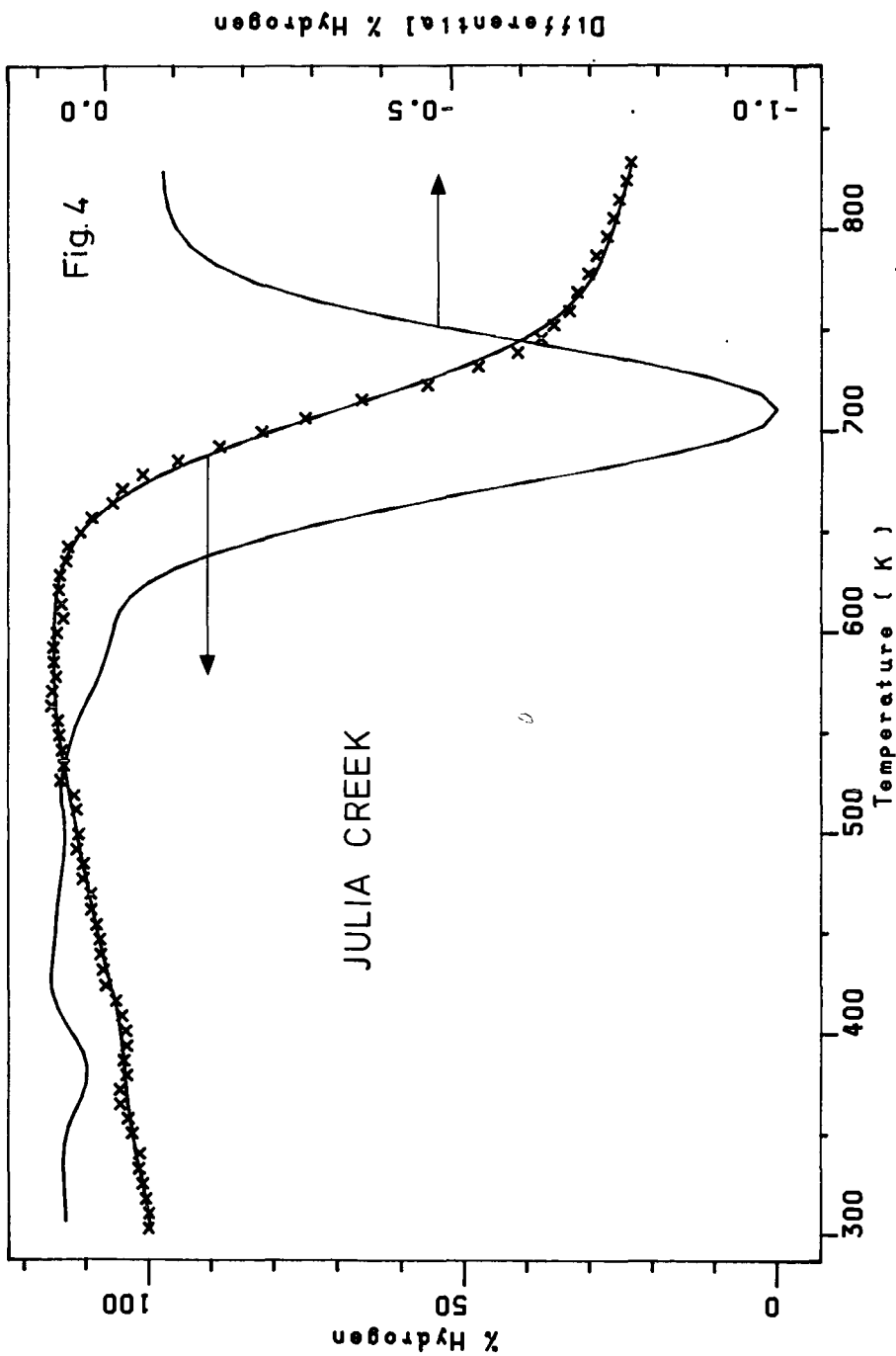
In comparing the ^1H NMR thermal scanning data of the whole and demineralized Julia Creek materials, we note the following. (a) A general similarity in the apparent hydrogen loss behavior but that the maximum rate of percentage hydrogen loss occurs sooner for the demineralized shale although the maximum rates are the same (Figures 4 and 5). (b) There is little difference in the behavior of M_2^* except that the demineralized shale acquires 'mobility' at a slightly earlier period. The same small minimum values of M_2^* are attained indicating the absence of rigid components in either structure (Figures 10 and 11). (c) The proportion of 'rigid' hydrogen falls to a lower value for the demineralized shale and there is a major difference in the variations of the T_2^* parameter. This parameter shows that a much greater molecular mobility is acquired by the 'mobile' fraction of the demineralized shale (Figures 8 and 9).

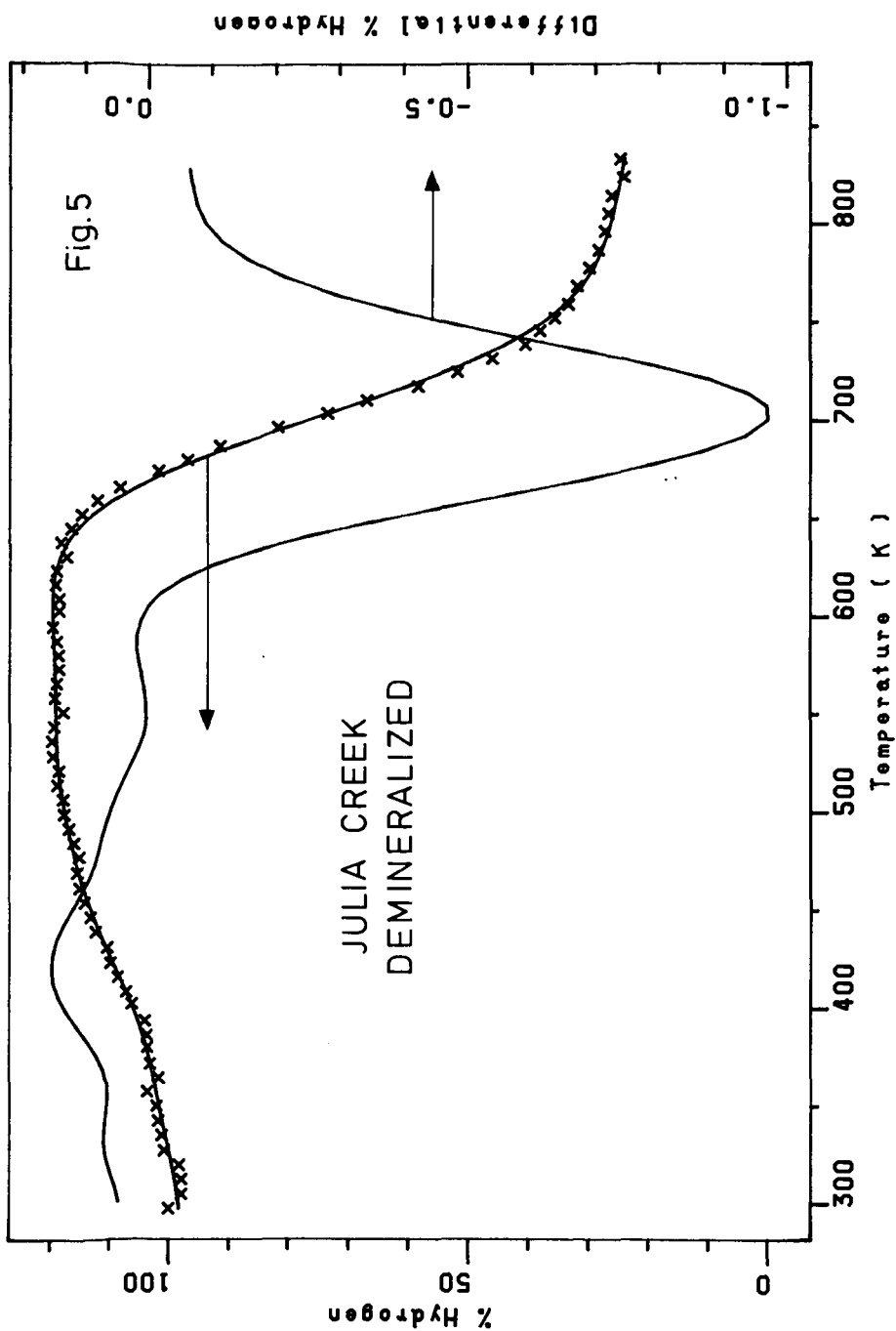
This comparison of the whole and demineralized Julia Creek shales shows that, although the degree of molecular mobility of the material 'softened' during the heating, is greatly inhibited











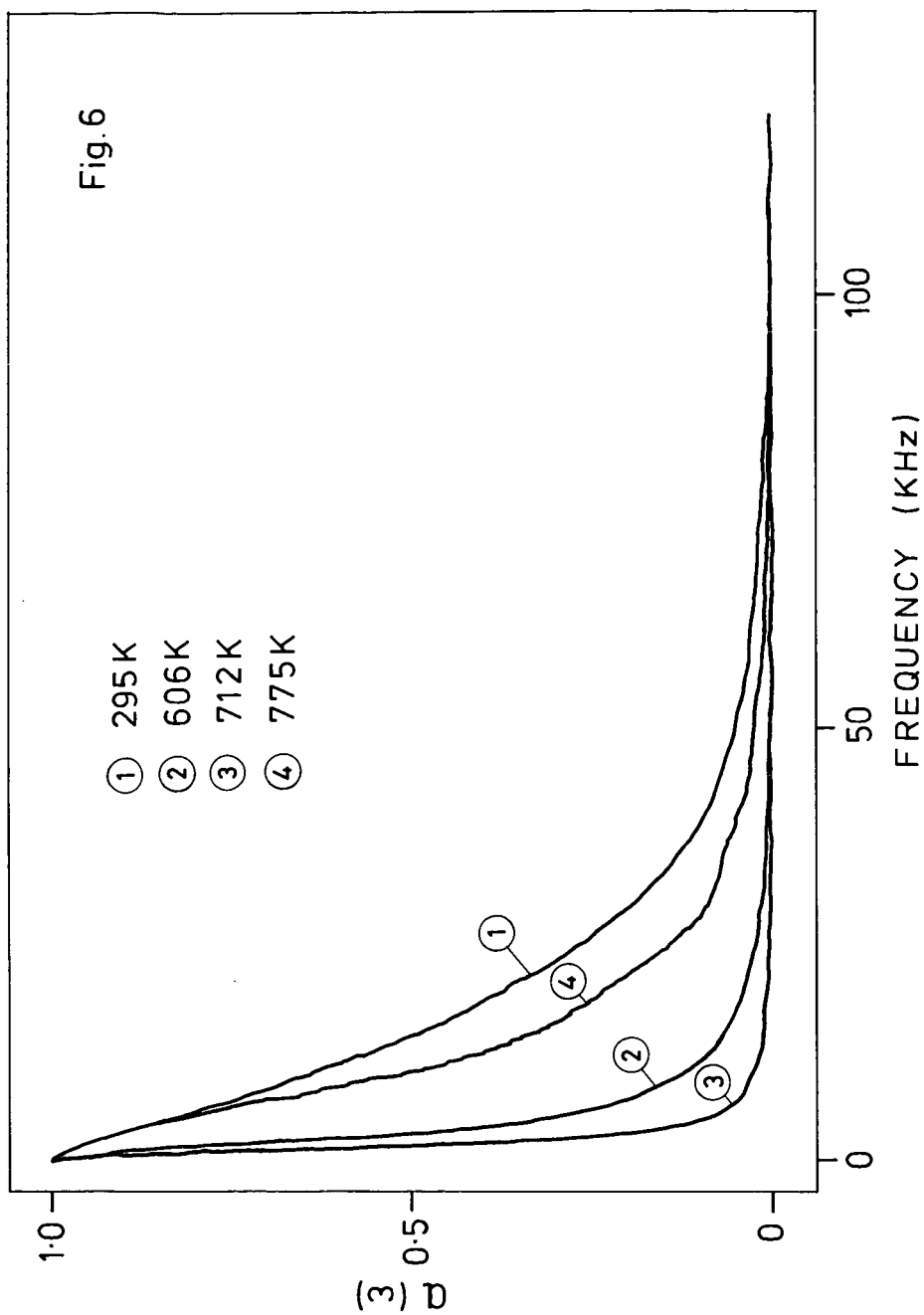
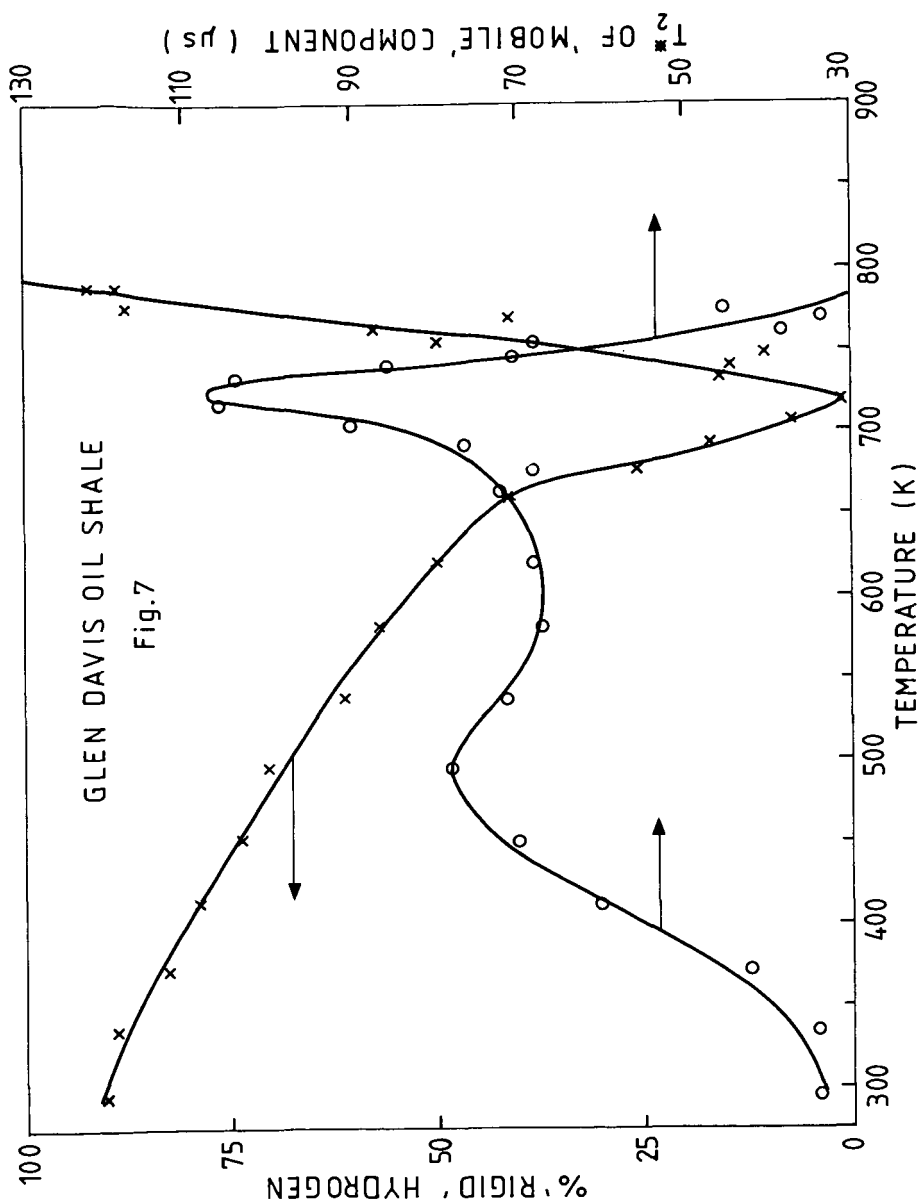
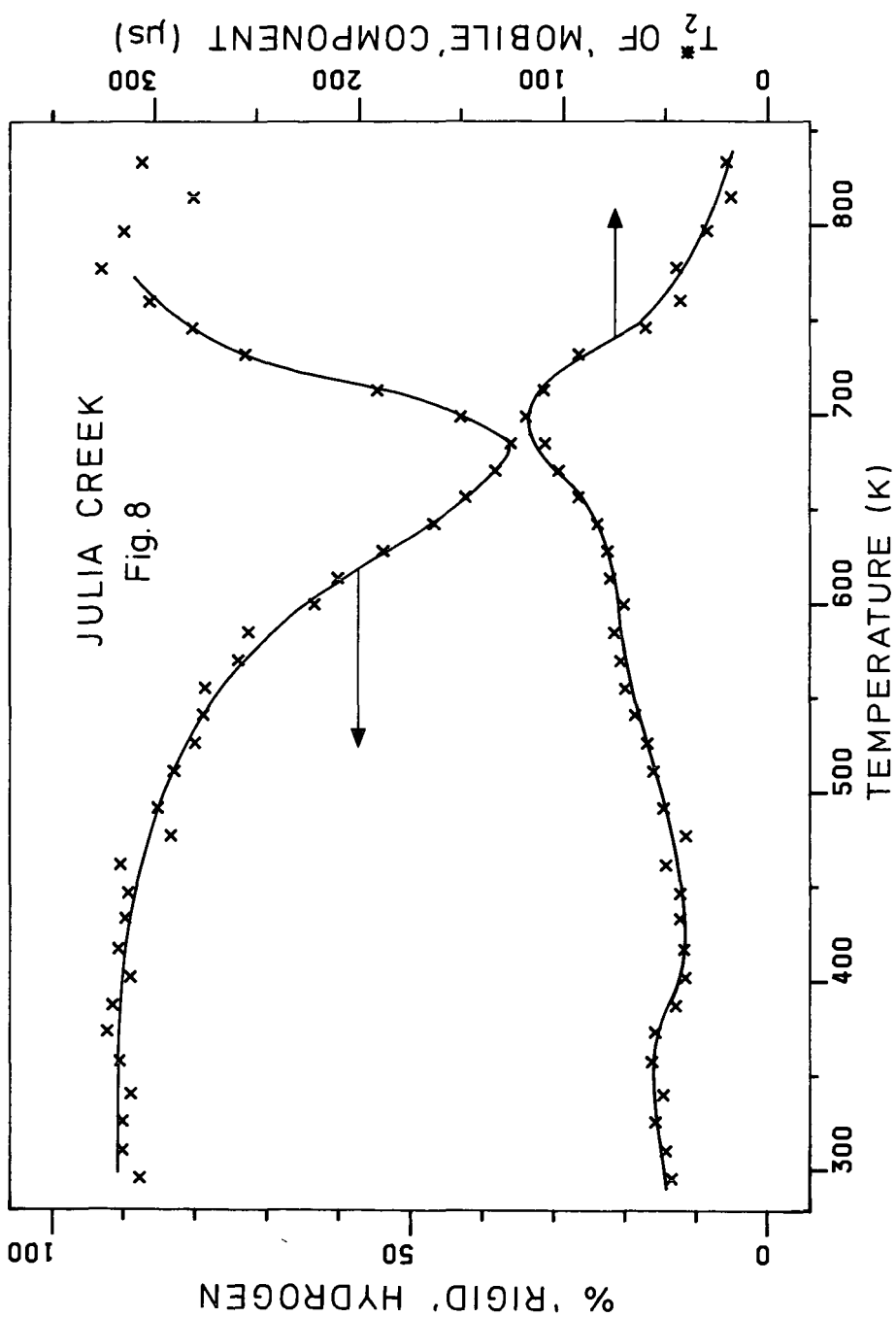
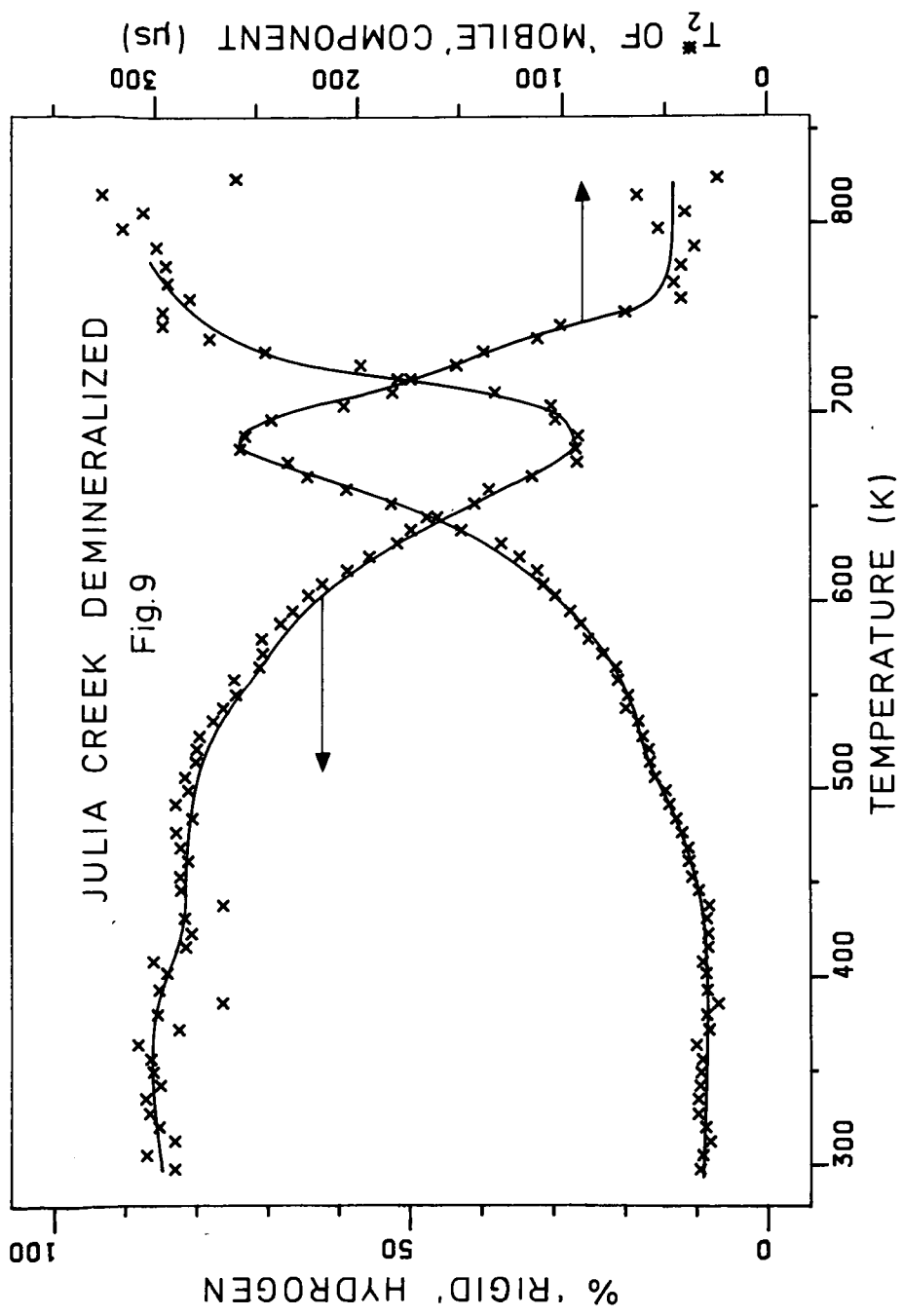


Fig. 6

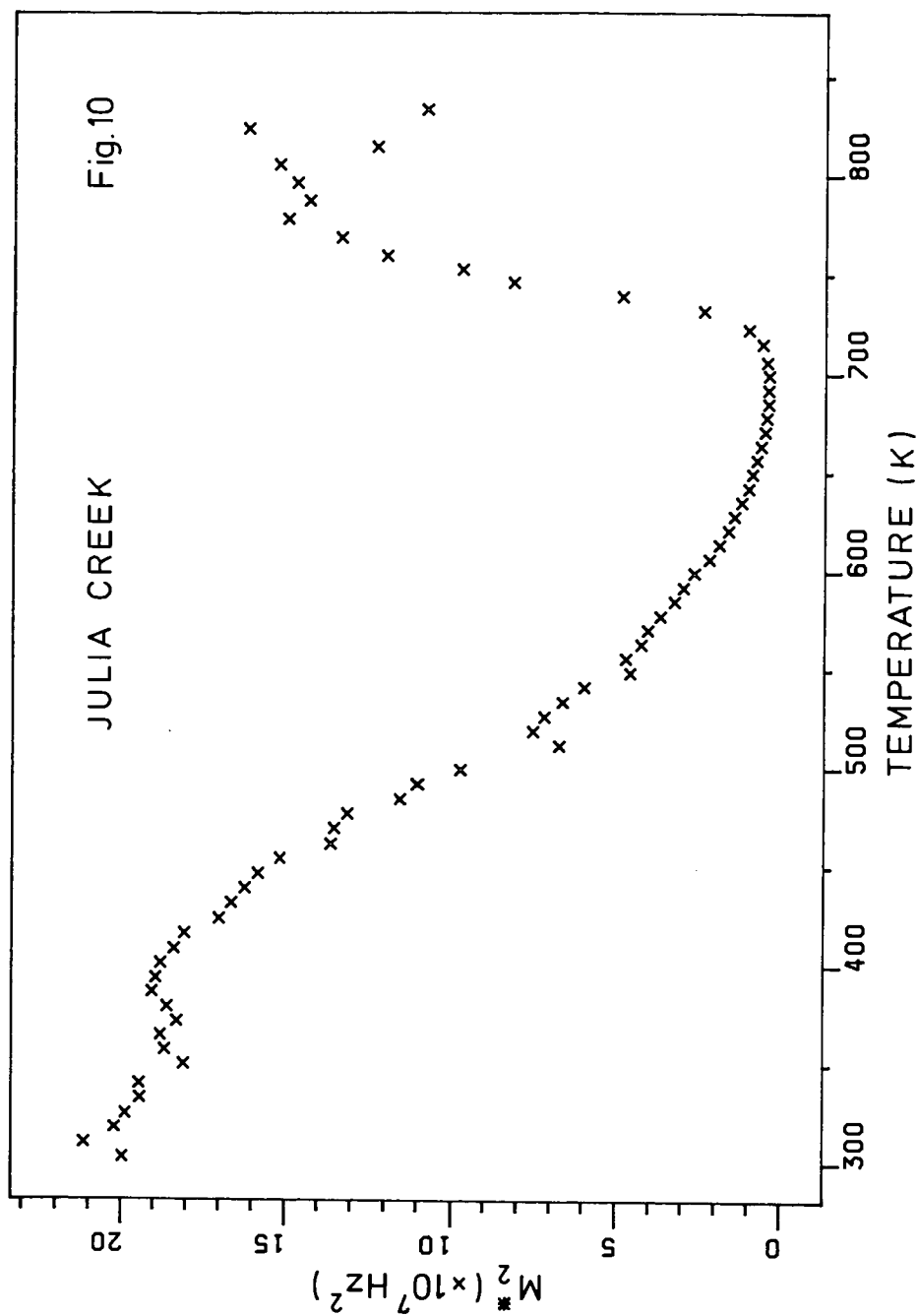


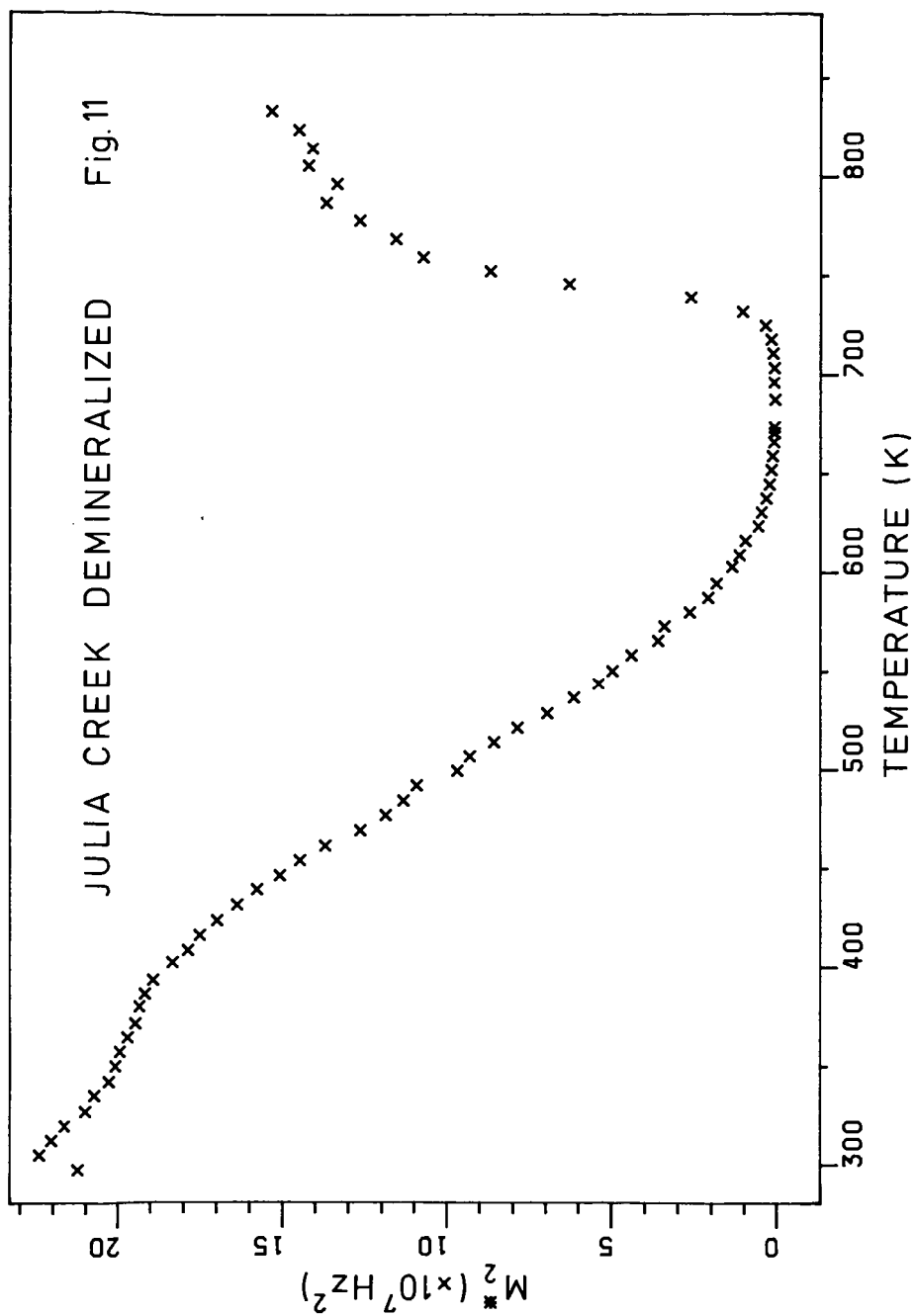




JULIA CREEK

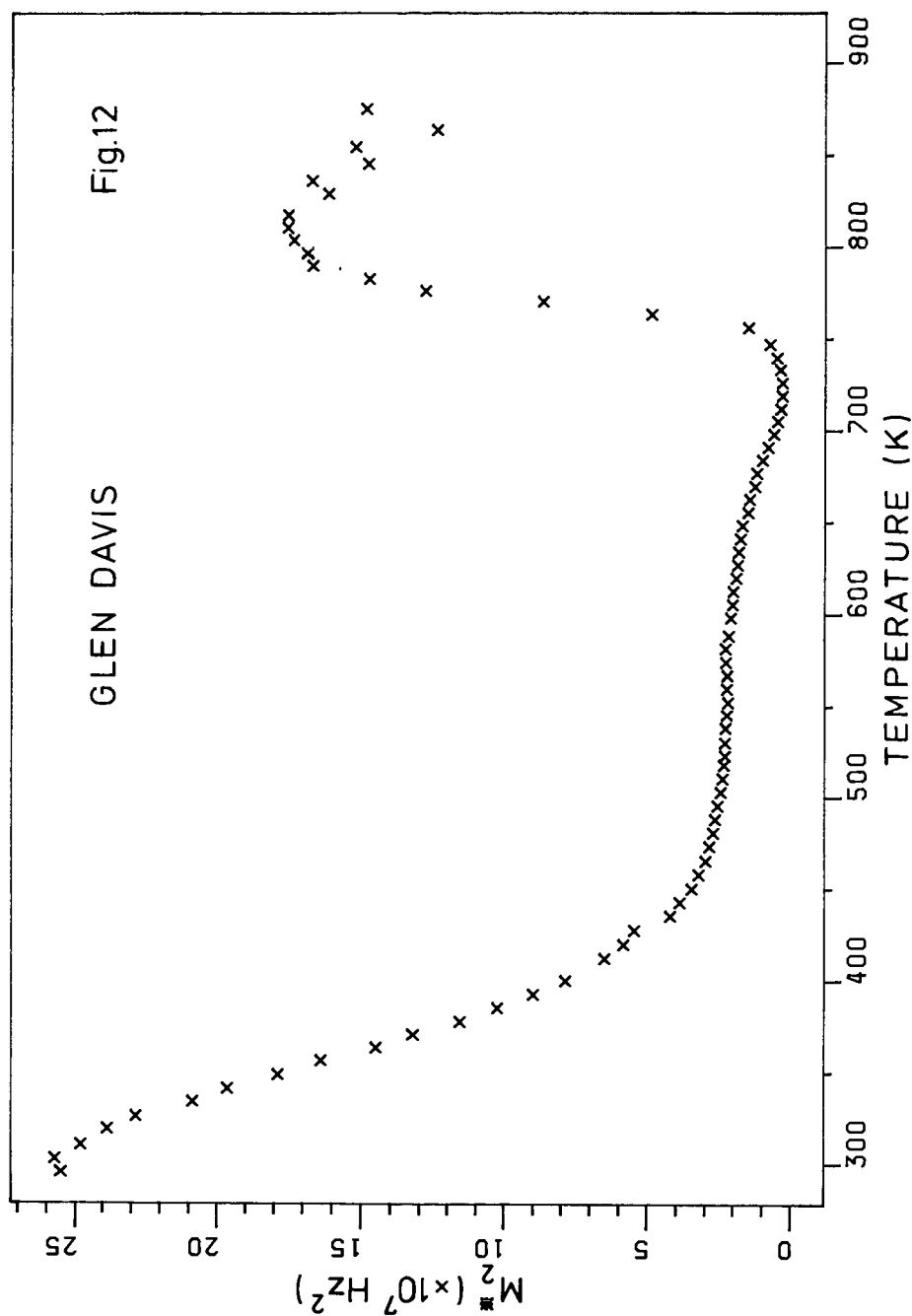
Fig.10





GLEN DAVIS

Fig.12



by the presence of the inorganic material it does not have much effect on the eventual thermal decomposition of the organic material.

The observations of Miknis et al (16) that the aromatic component of oil shales remain inert during pyrolysis does not appear to be the case for the shales studied here. This is apparent from the transient behavior of the molecular mobilities as indicated by the parameter M_2^* . The very low values of M_2^* achieved prior to the main pyrolysis zone clearly show that all significant components of the organic hydrogen in both the Julia Creek and Glen Davis shales pass through a highly mobile stage before a residual rigid lattice component is formed during the main pyrolysis periods. It is unlikely that the original aromatic materials in these shales could undergo the transient softening observed here without the occurrence of at least some chemical change as well as the obvious physical changes.

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